Thermodynamic properties in terms of the Partition function :— we can use the M-B distribution law and the related partition functions to calculate the macroscopic (thermodynamic) properties such as internal energy, enthalpy, entropy, free energy, etc., of matter.

Internal Energy :— The internal energy, E, of a system consisting of N independent particles is equal to the sum of the energies of individual particles. Thus,

$$E = \sum_i N_i \varepsilon_i = N\bar{\varepsilon} \quad \text{—— (1)}$$

where $\bar{\varepsilon}$ is the average energy of the particles defined by

$$\bar{\varepsilon} = \left(\sum_i N_i \varepsilon_i\right) \Big/ \sum_i N_i$$

$$= \left(\sum_i \varepsilon_i e^{-\beta G_i}\right) \Big/ \sum_i e^{-\beta \varepsilon_i} = \left(\sum \varepsilon_i e^{-\beta \varepsilon_i}\right) / q \quad \text{—— (2)}$$

Now

$$\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{\partial \left(\sum \varepsilon e^{-\beta \varepsilon_i}\right)}{\partial \beta} = -\sum_i \varepsilon_i e^{-\beta \varepsilon_i} \quad \text{—— (3)}$$

where the differenciation is carried out at constant volume since the energies ε_i depend upon the volume. Hence,

$$\bar{\varepsilon} = \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln q}{\partial \beta}\right)_V \quad \text{—— (4)}$$

Therefore from eqs (1) and (4) for a system containing N particles,

$$E = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V \quad \text{—— (5)}$$

Since $\beta = 1/kT$ and $Nk = nR$ (where n is the number of moles), we have.

$$E = nR\left(\frac{\partial \ln q}{\partial (1/T)}\right)_V = nRT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \quad \text{—(6)}$$

Molar Heat Capacity:- For one mole of a system ($n=1$), differentiation of E with respect to T at constant V, yields the molar heat capacity C_V. Hence

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = R\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial \ln q}{\partial T}\right)_V\right] = \frac{R}{T^2}\left[\frac{\partial^2 \ln q}{\partial (1/T)^2}\right]_V$$

Entropy:- If the particles are considered indistinguishable then the thermodynamic probability for the system must be divided by $N!$ to yield the new thermodynamic probability of the Boltzmann distribution then we get-

$$W = \Pi_i g_i^{n_i}/n_i! \quad \text{—(1)}$$

where W is thermodynamic probability and g_i is the degeneracy of i^{th} energy level. Now we know that entropy is related to the probability is given by the expression

$$S = k \ln W \quad \text{—(2)}$$

$$S = k\left(\sum_i n_i \ln g_i - \sum_i \ln n_i!\right) \quad \text{—(3)}$$

using the Stirling approximation

$$S = k\sum_i n_i \cdot \ln(g_i/n_i) + kN \quad \text{—(4)}$$

we know $\ln g_i/n_i = \ln(q/N) + \varepsilon_i/kT$ —(5)

Substituting eq (5) in eq (4) we have

$$S = k\sum_i n_i \ln\frac{q}{N} + k\sum_i \frac{n_i \varepsilon_i}{kT} + kN. \quad \text{—(6)}$$

or $$S = kN\ln\frac{q}{N} + \frac{E}{T} + kN$$

For n moles of the system $kN = nR$. Also using the expression for E ~~given~~ we have

$$S = nR\left[\ln\frac{q}{N} + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right] \quad \text{—(7)}$$

Enthalpy :- Enthalpy is given by relation

$$H = E + PV. \quad \text{—}$$

If we substitute here the energy expression we get

$$H = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V + PV$$

Helmholtz free energy (A) :- In thermo dynamics this is expressed as

$$A = E - TS$$

Substituting the energy expression and expression of entropy in the above expression, we have

$$A = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V - nRT\left[\ln\frac{q}{N} + \left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right] \quad \text{—(1)}$$

$$= -nRT(\ln q/N + 1) \quad \text{—(2)}$$

or $$A = -kT[\ln q^N - (N\ln N - N)] = -kT\ln(q^N/N!) \quad \text{—(3)}$$

Or $\boxed{A = -kT \ln Q}$

where Q is the molar Partition function i.e the partition function for one mole and q is the molecular partition function (Partition function a single molecule).

Gibbs function (G) :- It is defined as

$$G = H - TS = (E + PV) - TS = A + PV$$

~~Substituting the expression of A & and expression for P we obtain~~ :- Substituting the expression of A we obtain

$$\boxed{G = -nRT(\ln q/N + 1) + PV}$$

~~OR G = nRT~~

Also $\boxed{G = -kT \ln Q + PV}$

By : Dr. ANITA SINGH
Assistant Professor (Chemistry)
NGBU, Prayagraj (U.P.)-221505